

METHOD AND APPARATUS FOR THE PREPARATION  
OF HIGH PURITY PHOSPHINE OR OTHER GAS

5

Background Of The Invention

10 Field of the Invention

This invention relates to the chemical synthesis and production of semiconductor grade gases, such as phosphine, and a reactor for carrying out the synthesis. The synthesis and the reactor are designed to produce high purity gas and deliver it to a semiconductor fabrication process.

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Art Related to the Invention

High purity gases, such as phosphine ( $\text{PH}_3$ ), are required for semiconductor fabrication and doping. Phosphine is flammable, extremely toxic, and hazardous. Phosphine has a toxicity exposure limit of 0.3 ppm. Currently, the gas is manufactured in large centralized chemical plants and then delivered to semiconductor fabrication facilities in steel compressed gas cylinders. Compressed gas cylinders store this toxic gas at several thousand pounds per square inch pressure and contain one to forty five pounds of the gas. Hence, transportation, storage, and handling of these compressed gas cylinders present a major toxic gas release hazard to the environment and the workers within the semiconductor facility.

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On-site synthesis of these gases provides an alternative means to provide such gases to the semiconductor industry in a safe manner. The process and reactor described herein allows the gas to be generated on-site as needed thereby eliminating the transportation, storage, and handling of toxic gas cylinders in a semiconductor fabrication plant.

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The phosphine gas generator can be used for II-VI crystal growth including organometallic vapor phase epitaxy, and molecular beam epitaxy of InP, GaP, and solid state lasers such as those based on

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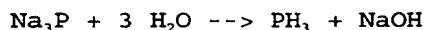
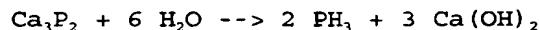
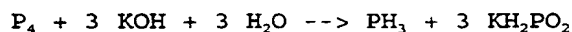
InGaAsP for fiber optic communications. In addition, the phosphine generator can be used as a dopant source for the silicon semiconductor fabrication.

5           The following references disclose processes for producing phosphine gas by chemical methods. Cotton and Wilkinson, Advanced Inorganic Chemistry, 4th Ed., Wiley Interscience (1980); Brauer, Preparative Inorganic Chemistry, Academic Press (1963); and Kirk-Othmer, Encyclopedia of Chemical Technology, Wiley Press.

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Phosphine is traditionally prepared by hydrolysis of white phosphorous or metal phosphides such as:

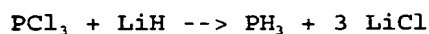
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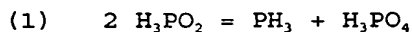
Phosphine can also be prepared by reducing phosphorous chloride with strong reducing agents such as lithium hydride:

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Other chemical reactions include thermal disproportionations. For example, upon heating above 120° C, hypophosphorous acid (H<sub>3</sub>PO<sub>2</sub>) disproportionates spontaneously to give phosphine and higher oxides of the phosphorous acid. By Thermal Gravimetric Analysis we have

30           determined that the principal reaction paths are:



35           which consist of the following component reaction paths:

130° C

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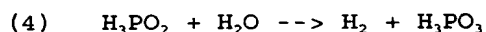


200° C

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5 A side reaction which is catalyzed by metals is



10 H.J. Banks and C.J. Waterford, U.S. Pat. No. 5,573,740, disclose a chemical method for generating phosphine based on the reaction of water or water vapor with a metal phosphide. W.Frierel and R. Ehert, U.S. Pat. No. 4,720,380 disclose an aluminum phosphide formulation for generation of phosphine for pesticidal applications. Both methods  
15 produce a dilute, moist phosphine for use as a pesticidal gas. This low concentration, impure gas is unsuitable for semiconductor applications.

C.R. Strauss and A.F. Faux, U.S. Pat. No. 5,387,397, disclose a  
20 method and apparatus for chemical reactions based on feeding reactants through a microwave-heated zone. This method is only appropriate for liquid phase or liquid slurry reactions in which the product is a liquid. No provision is made for phase change and gas product production and expansion within the reaction zone. Furthermore,  
25 Strauss's specification of a small diameter coiled tube in the microwave-heated region precludes refluxing of the chemical reaction in the heated region and hence limits the product yield.

Koch, in U.S. Patent No. 5,529,669 teaches the use of single  
30 mode microwave radiation to raise the temperature of a metal catalyst and thereby increase the reaction rate between ammonia and a hydrocarbon containing gas. Koch feeds two gas phase reactants over a microwave-heated catalyst. The product of the gas phase reaction is another gas, hydrogen cyanide. No phase change or allowances for  
35 phase change is taught in their patent. Furthermore no allowances are made for refluxing of reactants to increase the reaction yield of the products.

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T. A. Koch, K.R. Krause, and M. Mehdizadeh (U.S. Pat. Nos. 5,470,541 and 5,529,669) disclose a process for the preparation of hydrogen cyanide. Their method specifies a tubular reactor within a resonant cavity tuned to the TE011 mode of a microwave source.

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One major limitation of these inventions is the use of one material (Teflon or glass) as the conduit for exposing the reactants to microwave energy. This limits the type of reactions which can be carried out. Teflon is limited to temperature below 260° C and glass or quartz is attacked and corroded by hot alkali and some acid solutions.

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Summary Of The Invention

The present invention relates to a chemical process and reactor suitable for producing phosphine or other gases of sufficient purity and at a proper pressure, for direct introduction into a process in which semiconductors are manufactured or doped. These semiconductor manufacturing processes typically include a chemical vapor deposition reactor (hereafter CVD) used for epitaxial growth of phosphorous containing semiconductors or an oxidation furnace used for phosphine doping of semiconductors.

In one embodiment, the invention provides a preferred reactor that includes a source of microwave radiation, a microwave transparent, metal free, gas tight reaction zone or chamber, and a microwave reflecting enclosure. The gas is produced by the interaction of microwave radiation with a precursor material. The precursor preferably is a liquid but in broad aspects may also be a solid, e.g. crystalline  $H_3PO_2$  or crystalline  $H_3PO_3$  for the production of phosphine. Preferably, a liquid precursor such as a solution of an appropriate acid or salt passes through the microwave transparent reaction zone thereby allowing the production of the high purity chemical with minimal by-product reaction contamination. The preferred microwave source can be quickly turned on and off thereby allowing for rapid heating and cooling of the precursor material, and hence the rate of chemical reaction. The microwave radiation predominately heats the precursor with minimal heating of the surrounding containment chamber. In addition, a preferred device provides a phosphine generator having a phosphine source material canister or other container which desirably can be refilled with precursor material and recycled. This can minimize hazardous waste disposal and provide a responsible approach to protecting the environment for the phosphine production and utilization.

One feature of the invention is that it addresses the limitation of use of a single material, such as Teflon or glass, in the microwave heated zone, by the use of composite or multiple (e.g. two)

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layer microwave transparent conduits which provide a corrosion barrier and mechanical strength at high temperature and pressures. The preferred microwave transparent material in the reaction zone also is capable of sustaining pressures above one atmosphere and is resistant to corrosion from the chemicals within the reaction zone.

Other advantages of preferred embodiments of the invention include unexpected very high yield production of pure, hydrogen free, phosphine (>99.99%) by the elimination of all non-refractory metals from the reaction zone, and no need for tuned resonant cavity (less expensive to manufacture). We have found that the reactions occur with high selectivity without the need of the specific TE011 microwave radiation mode. In addition, in the reaction zone, liquid or vapor of the reacting material comes into contact with heated non-reacting fluid thereby accelerating heat transfer and the reaction process; very fast heat transfer to the reactant fluid. Still further, the preferred process and reactors provide for reflux of reactants within the microwave heated zone.

In more preferred embodiments, an automated pneumatic manifold for gas delivery can be used to direct the gas to the semiconductor reactor. Preferably located on the manifold are solvent vapor removal cartridges (e.g. containing silica gel) to remove traces of water from the gas, desirably to establish a product (e.g. phosphine) gas that contains no more than 100 parts per million of oxygen or water vapor. Also, a gas concentration sensor, and a feedback control system to control gas pressure and concentration, can be provided. A pressure sensor on the manifold and a microprocessor attached to it can be provided to maintain pressure in the reactor required by the inlet to the CVD to which it is connected, and to provide for suitable flow into it.

A concentration monitor on the manifold, a diluent gas mass flow controller, and a microprocessor attached to both can be used in a preferred apparatus to maintain the concentration of phosphine or other gas leaving the manifold at the desired value.

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The preferred system is automatically controlled by a microprocessor, and graphic interface based software. The software control on the system makes it easy to operate, purge and evacuate the system, and to deliver and blend phosphine in the concentration  
5 desired. The preferred software also displays the concentration of phosphine in the delivery gas stream in real time, tracks the amount of precursor material left in the supply tank, and displays the amount of phosphine or other gas available for delivery.

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An electrically grounded temperature probe sealed in Teflon and placed in the two-phase zone can be used to more accurately control the magnetron output without electromagnetic noise from the microwave.

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Two types of reaction chemistries may be utilized in the generation of phosphine. These are: thermal decomposition of acidic  $\text{H}_3\text{PO}_2$ , and base-catalyzed

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hydrolysis of red phosphorous which produces  $H_3PO_2$  as an intermediate compound leading to phosphine generation.

In another embodiment, the present invention provides a method  
5 for generating a high purity gas for semiconductor processing,  
comprising producing the gas by the interaction of microwave radiation  
with a precursor material while said precursor material passes through  
a microwave transparent, metal free, gas impermeable, pressurized  
reaction zone.

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The present invention also concerns a method for fabricating a  
semiconductor device using a gas, such as phosphine, characterized by  
the use of the gas when produced by the reaction of a precursor  
material under the influence of microwave radiation. In a preferred  
15 mode, such a method comprises producing the gas continuously by a  
continuous introduction and reaction of the precursor material in a  
microwave transparent reaction chamber irradiated with microwave  
radiation. and feeding the produced gas continuously as it is formed  
to a semiconductor fabrication process.

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In yet another embodiment, the invention provides an apparatus  
for the fabrication of a semiconductor device, comprising a gas  
generation reactor for generating a gas, the gas generation reactor  
having a microwave transparent reaction chamber and a source of  
25 microwave radiation directed into the reaction chamber, and a  
semiconductor fabrication device, such as a chemical vapor deposition  
reactor or an oxidation furnace, coupled to the gas generation  
reactor.

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Additional embodiments, features and advantages will be apparent  
from the disclosures herein.



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### Brief Description Of The Drawings

5           Figure 1 provides a diagrammatic view of a preferred reactor of  
the invention.

Figure 2 provides a diagrammatic view of another preferred reactor of the invention.

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Figure 3 provides a diagrammatic view of another preferred reactor of the invention.

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Description Of The Preferred Embodiments

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to  
5 embodiments thereof and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations, further modifications and applications of the principles of the invention as described herein being contemplated as would normally  
10 occur to one skilled in the art to which the invention pertains.

Referring now to FIG. 1, shown is a preferred reactor system of the invention. The reactor includes a reaction chamber tube 1 of a microwave transparent material (e.g. fused silica, silicon dioxide,  
15 boron nitride, graphite or Teflon) that is irradiated with microwave radiation from a radiation source including a magnetron 2 attached to a waveguide 3. This microwave radiation source may, for example, have a frequency of about 0.9 GHz or from about 2.41 to about 10 GHz. The reaction chamber 1 is contained within a microwave reflecting  
20 enclosure 4, for instance constructed of an electrically conductive material desirably having a conductivity of at least about  $10^{-3}$  ohm/cm. The enclosure 4 also preferably has a smallest dimension at least twice the wavelength of the microwave radiation to be employed. At the bottom of the reaction chamber 1 is a high boiling point liquid  
25 (HBPL) such as phosphoric acid or silicon oil which absorbs the microwave radiation.

A pump 5 transports a precursor material, preferably a liquid, from a feed source 6 into the reaction chamber 1 at a fixed or variable, preferably fixed, feed rate. The precursor material is  
30 capable of reacting in the reaction chamber 1 to produce a desired gas. In the production of phosphine, the precursor material may for example be an aqueous solution of  $H_3PO_2$ , an aqueous solution of  $H_3PO_3$ , an aqueous solution of a salt of the formula  $XH_2PO_2$  or  $XH_2PO_3$  wherein X is an alkali metal such as Li, Na or K, an aqueous solution of a salt  
35 of the formula  $Z_2(H_2PO_2)_2$  wherein Z is an alkaline earth metal such as Ca, Mg, Sr, or Ba, or an alkaline (e.g. aqueous NaOH, KOH or LiOH)

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slurry of red phosphorous. The precursor material flash evaporates and undergoes the disproportionation reaction to phosphine gas when it contacts the heated HBPL. The product phosphine gas and phosphoric acid expand in the tube as a foam with a void fraction of at least about 60%. The reaction chamber is sized to allow for this two-phase expansion.

One key feature of the expansion reaction zone is that it allows refluxing of the mixture. Refluxing within the chamber greatly increases the residence time and hence the yield of the reaction. The two-phase fluid refluxes in the reaction chamber until the reaction yield is at least 70% in preferred embodiments. The phosphine yield is a function of several factors, including the HBPL temperature, feed rate of the precursor solution, reflux, etc.

The preferred phosphine gas generation system can also be operated in a feed-back control mode to provide substantially constant pressure delivery of the gas, analogous to that described in WO 97/20965. In this mode, a pressure sensor 8 and a pressure regulator 9 can be mounted in the gas delivery line. A microprocessor 10 monitors the pressure signal and compares it to a desired set-point pressure. The microprocessor 10 then turns on or off the magnetron 2 to generate phosphine gas and maintain the desired set-point pressure. The microprocessor 10 can also control the sequencing of various valves or other components on the gas delivery manifold. For example, an automated pneumatic manifold for gas delivery can include a solvent vapor removal device or devices (e.g. cartridges containing silica gel) 7 to remove traces of water and/or other undesirable substances from the gas, desirably to establish a product (e.g. phosphine) gas that contains no more than 100 parts per million of oxygen or water vapor. The pressure sensor 8 on the manifold and the associated microprocessor 10 can be used to maintain pressure in the reactor required by the inlet to the CVD to which it is connected, and to provide for suitable flow of precursor material into it. A concentration monitor 11 on the manifold, a source of diluent gas 12, a valve 13, and a diluent gas mass flow controller 14, and the

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associated microprocessor can be used in a preferred apparatus to maintain the concentration of phosphine or other gas leaving the manifold at the desired value.

5           The temperature in the HBPL can also be detected by a platinum resistance temperature monitor (RTD) 15 electrically grounded to the magnetron power supply. This provides a steady temperature signal directly from the fluid without interference noise from the microwave radiation. The temperature of the HBPL can be maintained by a feed-  
10 back loop between the RTD and the microprocessor 10 connected to the magnetron power supply.

          The preferred system also includes graphic interface based software. The software control on the system makes it easy to  
15 operate, purge and evacuate the system, and to deliver and blend phosphine or other gases in the concentration desired. The preferred software also displays the concentration of phosphine or other gas in the delivery gas stream in real time, tracks the amount of precursor material left in the supply tank, and displays the amount of phosphine  
20 or other gas available for delivery. The microprocessor controller 10 is preferably remotely linked to a terminal device in a near-by or remote location.

          In another embodiment of the invention, the reactor may include  
25 an inner, corrosion-resistant microwave transparent tube is concentrically surrounded by a second microwave transparent tube capable of withstanding higher pressures. In this manner, higher pressures of phosphine can be produced safely without corroding the outer tube.

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          Figure 2 shows another embodiment of the invention. Here the microwave transparent reaction chamber tube is replaced with a microwave transparent flat window mounted on a steel reaction chamber. The reaction chamber 21 is a steel vessel capable of withstanding high  
35 pressures. The top of the chamber has a metal plate in which is mounted the microwave transparent window 22. The window 22 is fixed

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to the metal plate with an O-ring or other pressure-tight seal to prevent gas from escaping around the window 22. A wave guide 23 and one or more magnetrons 24 are mounted on the waveguide. Microwave radiation from the magnetron is directed through the microwave transparent window into the fluid 25 held in the reaction chamber.

The window can be made thicker and have a smaller area than the microwave transparent tube shown in Fig. 1. Both of these factors allow the window to withstand higher pressures than the tube configuration. By this means the temperature and pressure limitations of materials currently used in microwave transparent tubes or conduits in the reaction chamber are overcome. This allows higher pressure gas product to be produced with less concern of materials failure and gas leakage from the reactor. The inside of the reaction chamber can also be coated with a corrosion-resistant coating (e.g. tantalum or Tefzel), to eliminate contact of the hot fluid with the chamber walls.

In yet another preferred embodiment of the invention, Fig. 3 illustrates a microwave transparent reflux tube 31 extending partway up the height of a stainless steel vessel 32. Holes in the bottom of the reflux tube allow the HBPL to flow into a concentric outer container 33 thereby controlling the liquid height in the reflux tube. Reaction product phosphoric acid liquid overflows the edge of the outer container and exits the steel vessel through a drain 34. The reactant feed liquid is fed into the center tube 31 where it contacts the hot HBPL and flash evaporates. The reactant liquid and vapor reflux within the center tube until the reaction reaches completion. The product gas exits the steel chamber through a port 35.

It will be understood that the reactor systems illustrated in Figs. 2 and 3 can be equipped with similar manifold and control features to those illustrated in Fig. 1. Thus, the systems of Figs. 2 and 3 can include components corresponding to those numbered 7-15 in Fig. 1.

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The following examples illustrate, but do not define or limit, the invention.

EXAMPLE 1

5           One particular configuration for the process for producing phosphine is the thermal decomposition of  $\text{H}_3\text{PO}_2$ . Phosphine was generated using a vertical tubular reactor made of Teflon-PFA. The reactor had an inside diameter of 0.957 inch, outside diameter of 1.315 inch and total length of 35 inches. The reactor consists of  
10 three zones; an entrance zone (of length 8.5 inches), a microwave irradiated reaction and reflux zone (of length 10 inches) and an overflow zone (of length 16.5 inches). The extended zones of entrance and overflow were used to assist reactant reflux, cooling, and gas-liquid separation of the hot reaction products before they  
15 reach the exit port. The microwave transparent tube was irradiated with approximately 850 watts at 2.45 Ghz.

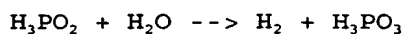
          The phosphine was generated at  $240^\circ\text{C}$  and 25 pounds per square inch outlet pressure. The rate of phosphine gas production proportional to microwave wattage heating the reaction zone. The  
20 liquid feed, 50%  $\text{H}_3\text{PO}_2$  in water, was pumped into the bottom of the tube at 2.6 and 10.8 milliliters/min. At the liquid feed rate of 2.6ml/min the conversion of  $\text{H}_3\text{PO}_2$  to  $\text{PH}_3$  was 94 % with a phosphine production rate of 260 standard cubic centimeter per minutes (sccm). At a feed rate of 10.8 ml/min the conversion was 73 % with a  
25 phosphine production rate of 850 sccm. In both cases, the purity of the phosphine was greater than 99.99%.

          During microwave heating of the liquid, about 75% of the reactor volume is filled with a two-phase gas liquid foam consisting of phosphorous acids, water vapor, and phosphine. The two-phase  
30 foam refluxes in the reaction zone until it some of it overflows out of the phosphine exit port on the tube. At the end of the production run, the solution remaining in the reactor tube consists over 90%  $\text{H}_3\text{PO}_4$  in water. This solution is used as the high boiling point liquid heating medium.

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By keeping the reaction zone free of metals (including stainless steel and Inconel), extremely high purity, hydrogen free, phosphine was produced. By-product hydrogen can be produced by the reaction:

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which we have found is catalyzed by transition metals.

#### EXAMPLE 2

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In this example, the raw material for production of high purity phosphine gas consists of a finely divided slurry of red phosphorous powder. Red phosphorous, is a polymeric form of white phosphorous. It is stable in air and water and therefore much safer to use as a precursor material than white phosphorous. We mixed red phosphorous powder (100 mesh size) into a potassium hydroxide solution to produce a slurry. Upon microwave heating of the slurry, we found the following reactions occur:

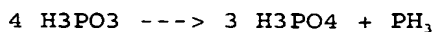
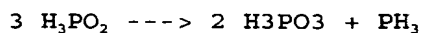
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The hypophorous compound can be further decomposed as in Example 1

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By varying the concentration of KOH between 5 and 11 molar and the temperature between 42 and 85° C, we determined that the rate of phosphine generation from this reaction can be described by the equation:

$$\text{rate} = k_0 \cdot \exp(-13,780/RT) \cdot [\text{OH}^-]^3$$

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where  $k_0 = 0.55$  and rate is expressed as moles of  $\text{PH}_3$  produced per gram of red phosphorous per second of reaction time. By this means we have found that one standard liter per minute of  $\text{PH}_3$  can be produced by the thermal reaction of 34.4 grams of P(red) per minute

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at 85° C. Faster production rates of phosphine can be produced at higher temperatures up to the material limits of the reaction zone material.

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EXAMPLE 3

In a modification of the process, some applications for semiconductor growth may require a different phosphine concentration than produced by the generator. With conventional gas cylinders, different gas concentrations would have to be pre-mixed to the desired concentration before filling the gas cylinder. In a modification of the phosphine generator, a feedback loop is used to control the mixing of the two gases and thereby maintain the desired gas concentration. This makes phosphine generator more versatile in that it can provide a wide range of gas concentrations.

15 The operator of the phosphine generator desires to provide 50% phosphine in hydrogen to the CVD deposition reactor. The operator selects this desired concentration from the software program. The microprocessor then determines the concentration of phosphine flowing through a concentration sensor. The computer program  
20 compares this concentration to the set point or desired concentration. A mass flow controller (MFC) then allows a diluting gas, hydrogen, to flow into a mixing tee where it is completely mixed with the phosphine.

The mixed gas then enters the concentration monitor with the  
25 mixed final concentration is determined. The MFC is then directed by the PC program to increase or decrease the diluent flow to maintain the set point concentration value. By this means, the operator can set and control any concentration between 0% and the maximum phosphine concentration produced by the generator.

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